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TNO report

TNO-DV 2007 A028

**Present state of CBRN decontamination
methodologies**

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Stand van zaken CBRN-ontsmettingsmethodieken

Het rapport presenteert een overzicht van de gangbare ontsmettingsmethodieken en de nieuwste ontwikkelingen binnen het vakgebied besmettingsbeheersing.



Probleemstelling

Om de gevolgen van een incident met chemische, biologische en radiologische / nucleaire (CBRN) agentia te beperken, kunnen militaire troepen gebruik maken van een reeks ontsmettingsmethodieken.

Idealiter zou een ontsmettingsmiddel effectief zijn tegen alle CBRN-agentia, geen materialen aantasten, kant-en-klaar, milieuvriendelijk, goedkoop en niet giftig zijn. Aangezien een middel dat al deze eigenschappen bezit nog niet bekend is, wordt wereldwijd continu onderzoek gedaan naar nieuwe en verbeterde

ontsmettingsmethodieken. Dit rapport geeft een overzicht van de gangbare methoden en de nieuwste ontwikkelingen. Het rapport voorziet in deliverable 4.2.6 van onderzoeksprogramma V502.

Beschrijving van de werkzaamheden

Er werd een literatuurstudie verricht naar de huidige stand van zaken omtrent CBRN-ontsmetting. Geraadpleegd werden: wetenschappelijke literatuur, presentaties die zijn gehouden op internationale congressen en informatie van leveranciers.

Resultaten en conclusies

In het rapport wordt onderscheid gemaakt tussen fysieke, chemische, enzymatische en energetische ontsmetting. Het hoofdstuk over chemische ontsmetting is het meest omvangrijk. De werkingsmechanismen van de methodieken wordt beschreven, evenals de voor- en nadelen ten aanzien van de toepasbaarheid, en de commerciële status. Van iedere methode wordt, voor zover bekend, aangegeven wat de toepassing is voor CBRN-agentia en toxische industriechemicaliën (TICs).

Toepasbaarheid

Dit rapport is bruikbaar om onderzoek te sturen en voor de behoeftestellers binnen Defensie.

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Abbreviations

| | |
|-------|--|
| APD | Atmospheric plasma decontamination |
| BC | Biological and chemical |
| BWA | Biological warfare agent |
| CARC | Chemical agent resistant coating |
| CBRN | Chemical, biological, radiological and nuclear |
| COTS | Commercially off the shelf |
| CWA | Chemical warfare agent |
| DETA | Diethylenetriamine |
| DIASH | 2-(Diisopropylamino) ethanethiol |
| DS-2 | Decontaminating Solution Number 2 |
| DSTL | Defence Science and Technology Laboratories |
| ECBC | Edgewood Chemical Biological Center |
| EDS | Electrostatic Decontamination System |
| EGME | Ethylene glycol monomethylether |
| EMPA | Ethyl methyl phosphonic acid |
| GB | Sarin |
| GD | Soman |
| HD | Sulphur mustard |
| IMPA | Isopropyl methylphosphonic acid |
| mVHP | Modified vaporized hydrogen peroxide |
| NaDCC | Sodium dichloroisocyanurate |
| OP | Organophosphate |
| PAA | Peracetic acid |
| PMPA | Pinacolyl methylphosphonic acid |
| RN | Radiological and nuclear |
| RSDL | Reactive skin decontamination lotion |
| SED | Sensitive equipment decontamination |
| STB | Supertropical bleach |
| TDG | Thiodiglycol |
| TICs | Toxic industrial chemicals |
| VHP | Vaporized hydrogen peroxide |

Summary

Decontamination is defined as the removal and/or neutralization of chemical, biological, radiological and/or nuclear (CBRN) contamination. In this report, the present state of the art of decontamination technologies is discussed. Advantages and disadvantages of the available methods are given, as well as the applicability towards CBRN agents and toxic industrial chemicals (TICs) and the commercial availability of decontaminants. Decontamination methods are divided into four basic processes: physical, chemical, enzymatic and energetic decontamination.

Physical methods aim at removing the contaminants from surfaces and include weathering, rinsing with water and solvents, accelerated evaporation by heating, and the use of solid adsorbents and strippable coatings. In principle, RN decontamination can only be obtained through physical removal and containment.

Chemical, enzymatic and energetic methods aim at modifying the structure of contaminants in order to reduce or eliminate the toxicity of the compounds.

The following chemical decontamination methods are discussed: oxidation (chlorine, peroxides and reactive gasses), nucleophilic substitution (alkaline hydrolysis and oximes) and alternative chemical approaches. Some chemical decontaminants are effective but highly toxic and environmentally unsafe. An example is DS-2, that is currently being replaced by safer decontaminants such as, in The Netherlands, GDS2000.

An environmental friendly alternative for aggressive chemical decontaminants was found in the use of enzymes. Some enzymatic decontaminants are commercially available. Most enzymes are only effective against GB and GD, however, some enzymatic approaches towards destruction of VX, HD and BWAs have been reported. Finally, directed energy methods, such as photochemical, ultra violet radiation, plasma, and microwave radiation have all been demonstrated to disinfect surfaces.

However, these methods are not generally applicable.

Unfortunately, there is no single decontamination technology that is effective against all CBRN agents. Therefore, there are still sufficient challenges for further innovative developments in the future.

Contents

| | | |
|----------|--------------------------------------|-----------|
| | Managementuittreksel | 2 |
| | Abbreviations | 4 |
| | Summary | 5 |
| 1 | Introduction | 7 |
| 2 | Decontamination methods | 8 |
| 2.1 | Physical decontamination | 8 |
| 2.2 | Chemical decontamination..... | 10 |
| 2.3 | Enzymatic decontamination..... | 20 |
| 2.4 | Directed energy decontamination..... | 21 |
| 3 | Concluding remarks | 22 |
| 4 | References | 23 |
| 5 | Signature | 27 |

1 Introduction

As defined in the Decontamination Tryptich of the NATO [1], decontamination is the removal and/or neutralization of chemical, biological, radiological and/or nuclear (CBRN) contamination. In this report, the present state of decontamination technologies is discussed. This report was written as part of research program V502 'Passive protection against CBRN weapons' on behalf of the Dutch Armed Forces. The report will be annually updated with new developments, for the duration of the Program (2006-2009).

Decontamination methods can be divided into four basic processes: physical, chemical, enzymatic and energetic, which are treated in Sections 2.1 to 2.4, respectively.

Physical methods aim at removing the contaminants from contaminated surfaces, whereas chemical, enzymatic and energetic methods aim at modifying the structure of the contaminants in order to reduce or eliminate the toxicity of the contaminants.

For chemical agents this modification is a change in the chemical structure of the agent molecules, for biological contaminants this is the destruction of the cells.

Traditional decontamination technologies all have drawbacks that led to the continuous search for improved methodologies. The ideal decontaminant (or the 'silver bullet') should be non-aggressive, non-toxic, environmentally friendly and not destructive to materials. It will destruct all biological and chemical (BC) agents at the same time and removes radiological and nuclear (RN) agents. It will preferably be ready to use without the need of previous mixing of various ingredients in the field, and it should place a minimal logistic burden in terms of storage and transportation requirements.

Currently there is no single technology that meets all these requirements [2].

It is important to realize that the decontamination efficiency depends on various factors, not only the characteristics of the agent, but also the weather conditions and the type of material that is contaminated. Smooth surfaces painted with chemical agent resistant coating (CARC) are relatively easy to clean with an effective decontaminant, whereas the same decontaminant may not be able to sufficiently clean more complex structures with cracks or crevices or absorbing materials such as rubber.

This report addresses currently available decontamination technologies and recent developments. Advantages and disadvantages of the available methods are given, as well as the applicability towards CBRN agents and toxic industrial chemicals (TICs). Furthermore, the commercial status of decontamination techniques is given.

2 Decontamination methods

2.1 Physical decontamination

Physical decontamination consists in either removing (relocating) or encapsulating contaminants without actual destruction of the agents. All materials used for the physical removal of CB agents need to be treated as contaminated waste. The following examples of physical decontamination will be discussed:

- weathering;
- rinsing with water;
- rinsing with organic solvents;
- accelerated evaporation by heating (hot air);
- adsorption and removal with solid adsorbents (e.g. Fullers earth);
- removal by strippable coatings.

Without any form of active decontamination, chemical agents will eventually attenuate over time by evaporation and natural destruction (weathering), depending on the characteristics of the agent, the weather conditions and the type of material that is contaminated. In case of, for instance, terrain contamination with chemical warfare agents (CWAs), a simple and cheap method would be to isolate the terrain, however, this is only feasible for remote areas. Studies have shown that within 3-5 days after terrain (soil and concrete) contamination with soman (GD), VX, and sulphur mustard (HD), the agents had degraded to non-hazardous levels [3-4, cited in 5]. The data suggest that in the locations studied, there would be no need for decontamination of GD or VX after 3 days and of HD after 5 days. However, CWAs may bind to soil particles and concrete. A study on the agent fate of VX on concrete showed that VX absorbed rapidly into concrete, after which it slowly hydrolyzed (half-life 3 months) [6]. Furthermore, organophosphorous (OP) pesticides, which have chemical properties that are comparable to nerve agents, are detected in soils years after application, which could only be explained by sorption [7].

Biological warfare agents (BWAs) are killed more rapidly outdoors, especially under the influence of sunshine. However, sporulated bacteria are more resistant to UV radiation than non-sporulated bacteria. Weathering is not possible for radiological and/or nuclear (RN) contaminants which may have half-life times of tens to hundreds of years. Without active decontamination, remote areas contaminated with radiological agents should be permanently isolated.

The most simple active decontamination method is rinsing contaminated surfaces with water to remove CBRN agents. The efficiency of rinsing methods will increase using high pressure, hot water, soap and brushes. Water will very slowly detoxify some CWAs by hydrolysis. Chemical agents tend to show greater affinity to organic compounds and thus rinsing with organic solvents normally results in improved physical removal. In addition, organic solvents also allow the extraction of ad-/absorbed agents from porous materials but may, as a result, damage certain substrates and/or coatings. Sensitive equipment that will become damaged after contact with water, may be decontaminated using organic solvents, e.g. fluorosolvents [8]. Batelle (Aberdeen, MD) designed a prototype of a modular sensitive equipment decontamination (SED) device. The process consists of ultrasonic solvent washing to remove BC agents followed by vacuum drying. The total process takes less than 20 minutes [9].

In principle, RN decontaminants can not destroy the radiation of RN agents, but are effective in physical removal and containment. Various decontaminants were developed for this purpose. Current commercially off the shelf (COTS) RN decontaminants mainly consist of aqueous mixtures containing surfactants and complexants. Examples are Decon90 (Decon Laboratories, King of Prussia, PA), Count-off (Perkin Elmer, Boston, MA), RDS2000 (Kärcher, Winnenden, Germany) and RN foam (OWR, Elztal-Rittersbach, Germany). It is recognized that some BC decontaminants partly constitute of surfactants and may therefore also be effective RN decontaminants (see Section 2.2). Recent RN decontamination experiments performed at TNO Defence, Security and Safety [10] showed that it will be difficult to develop a decontaminant that is capable of removing all types of radionuclides. It was shown that in the absence of a suitable decontaminant, water and scrubbing provide a good alternative for a substantial removal of radionuclides. When removal of RN agents is not effective on, for instance, porous surfaces, the only alternative will be to remove the contaminated surfaces (e.g. by sandblasting or grinding).

Thermal desorption of CWAs can be achieved by the use of heated air which results in evaporation of the contaminant. With this method, the toxic agent is released into the atmosphere and this may present an increased vapour hazard. The technique may, for instance, be utilized for the cleaning of clothing. Furthermore, micro-organisms (BWAs) are also killed by heat treatment.

Solid adsorbent decontaminants are very useful in removing CW contaminants from surfaces. Activated carbon, certain polymer ion-exchangers and fuller's earth (a claylike substance rich in minerals) are typical examples of solids that adsorb agents and retain them, allowing for safe removal and subsequent disposal. The usefulness of solid compounds for the decontamination of large equipment or vehicles is limited due to the problems of application over large surface areas.

Strippable coatings can basically be used in two ways for decontamination purposes. When a plastic membrane or coating is sprayed on the surface, the resulting coating may seal and contain the contaminants for a period of time if required. Contaminants will be removed when the coating is stripped off the surface. Alternatively, the coating may protect clean surfaces from becoming contaminated. The next step is to peel off the coating, thus removing loose surface contaminants. This process has been extensively used in the nuclear power industry. Isotron Corporation (Seattle) [11] has developed various strippable coatings for military use to contain (radiological) contaminated spread, to prevent objects from becoming contaminated and to decontaminate porous surfaces. At the Defence Science and Technology Laboratories (DSTL, Porton Down, UK), a binary approach was developed using peelable coatings that are removed after initial contamination in combination with decontaminants [12]. Laboratory test showed that most of the liquid CWA was absorbed by the coating on contact, leaving a small but significant residual contamination that had to be cleaned by a liquid decontaminant before stripping of the coating. This procedure led to a reduction in CWA contact hazard.

Peelable coatings are especially useful on geometrically complex surfaces that would otherwise lead to the entrapment of agents (underneath screws etcetera).

Although not a physical decontamination method, a related topic is the development of anti-microbial coatings which are able to destruct BWAs. The present state of the art on anti-microbial polymers is outlined in a separate report [13].

2.2 Chemical decontamination

Chemical decontaminants are substances that react with BC agents and transfer them into less or non-toxic substances. For CWAs this means a change in the chemical structure of the agent molecules, for BWA contaminants this is the destruction of the cells. As stated before, RN agents can not be destructed and can only be physically removed from contaminated objects. However, some BC decontaminants are effective in the removal of RN material.

Most of the current BC decontaminants can be considered reactive chemicals. Often, as in the case of oxidation or hydrolysis of chemical agents, the reactions occur immediately with the evolution of heat and gases. Reactive compounds will interact with metallic containers and coated surfaces to corrode the surfaces, and with human, animal and vegetative tissues to damage the tissues.

In this chapter, the following chemical decontamination methods will be discussed:

- oxidation;
 - chlorine based decontaminants;
 - peroxides;
 - reactive gasses.
- nucleophilic substitution;
 - alkaline hydrolysis;
 - oximes.
- alternative chemical approaches;
 - metal ion catalyzed hydrolysis;
 - reactive sorbents;
 - nanoactive particles.

General reaction mechanisms are given for the destruction of CWAs through oxidation and nucleophilic substitution.

2.2.1 Oxidation

2.2.1.1 Reaction mechanism

The reaction schemes of oxidation of HD, VX, sarin (GB) and GD are shown in Figures 1 to 3. Both HD and VX contain sulfur atoms that are readily subject to oxidation. Figure 1 shows how HD is oxidized into its sulfoxide (HDO) which has low toxicity, and its sulphone (HDO₂) which is a vesicant comparable to HD. The oxidized compounds react through elimination of HCl to produce the corresponding monovinyl and divinylsulfoxides and sulfones, although small amounts of additional unidentified products are also present in the final solution [14].

Upon cleavage of the P-S bond, VX is oxidized into the non-toxic products ethyl methyl phosphonic acid (EMPA) and 2-(diisopropylamino) ethanethiol (DIASH) (see Figure 2). The G agents GB and GD are oxidated by cleavage of the P-F bond, resulting in the formation of the non-toxic products isopropyl methylphosphonic acid (IMPA) and pinacolyl methylphosphonic acid (PMPA), respectively.

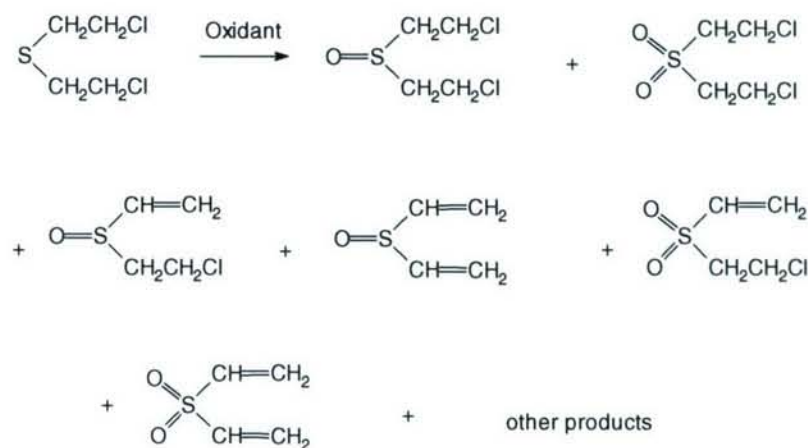


Figure 1 Oxidation of HD into its sulfoxide, sulfone and corresponding monovinyl and divinylsulfoxides and sulfones.

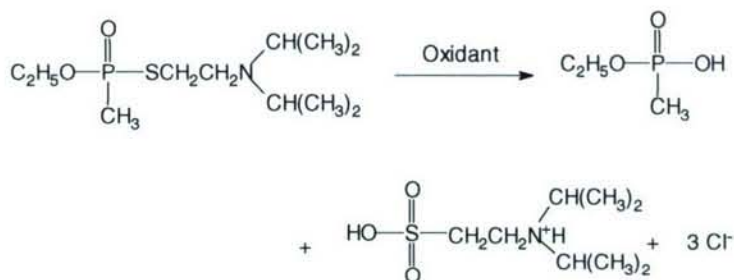


Figure 2 Oxidation of VX into ethyl methyl phosphonic acid (EMPA) and 2-(diisopropylamino) ethanethiol (DIASH).

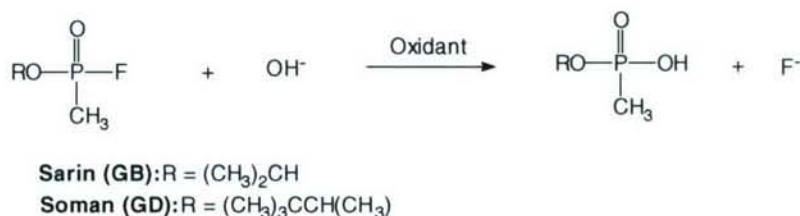


Figure 3 Oxidation of sarin and soman into isopropyl methylphosphonic acid (IMPA) and pinacolyl methylphosphonic acid (PMPA), respectively.

2.2.1.2 Chlorine based decontaminants

Sodium hypochlorite (NaOCl, common bleach) and calcium hypochlorite (Ca(OCl)₂, chlorinated lime or bleaching powder) were among the first oxidants used in chemical decontamination processes for BC agents and are still in use today. Hypochlorite ions (HOCl, hypochlorous acid or active chlorine) are generated by an alkaline aqueous solution of NaOCl or Ca(OCl)₂. The compound is effective in the decontamination of most BC agents but is corrosive to surfaces. Besides the degradation of CWAs (see Figures 1 to 3), HOCl in solution will oxidize many organic and inorganic toxic industrial chemicals (TICs) in water, including ammonia, organic nitrogen compounds (amides, amines, etcetera), multiple C-C bonds, and cyanides. HOCl is also a powerful

disinfectant. It is able to penetrate through the (bacterial) cell wall in a similar way to water. It is generally considered that the lethal action of HOCl after diffusion through the cell wall on organisms is due to the chlorination (oxidation) of cell proteins or enzyme systems. The biocidal activity of free available chlorine is influenced by various factors such as the pH (higher activity at low pH) and temperature (higher activity at high temperature) [15].

Supertropical bleach (STB) is a combination of $\text{Ca}(\text{OCl})_2$ and a strong base, calcium oxide (CaO, which produces the OH^- in solution). STB is effective in the detoxification of HD, G agents, and VX. However it does not effectively decontaminate HD if it has solidified at low temperature.

Other compounds that release active chlorine (so-called chlorine donors) are Chloramine-B and sodium dichloroisocyanurate (NaDCC, also known as Fichlor) (see Figure 4).

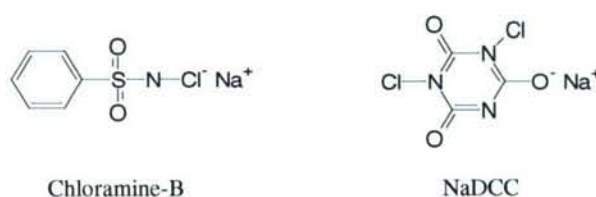


Figure 4 Molecular structures of Chloramine-B and sodium dichloroisocyanurate (NaDCC).

Chloramine-B is less aggressive than hypochlorite and is used to decontaminate personnel. The American personal decontamination kit M258, M258A1 and M280 contains wet towelettes impregnated with Chloramine-B. The compound is effective against HD and VX, but ineffective against the G agents and some biological agents. NaDCC is present in various decontaminants, such as BX24, a powder that easily mixes with water and is commercially available from Cristanini S.p.A. (Rivoli Veronese, Italy). OWR (Elztal-Rittersbach, Germany) offers a solution of 10% NaDCC in water for terrain decontamination. NaDCC is present in various formulations such as BC emulsion (produced by OWR) (see below).

CASCAD (Canadian Aqueous System for Chemical-Biological Agent Decontamination, Allen-Vanguard, Ottawa Ontario, Canada) [16] contains several surfactants in a proprietary mixture in combination with NaDCC as an active ingredient. The mixtures are supplied as a powder (NaDCC) and liquid, packaged separately. When combined, a foam is generated that is sprayed on the equipment to be decontaminated. The foam is able to contain and eliminate BC agents and remove radioactive particle contamination. A unique feature of the technology is the ability to use water from a variety of sources. The foam is equally active using distilled water, tap water, non-potable water, and even seawater. In some countries, e.g. Switzerland, CASCAD was chosen as the replacement for DS-2 (see Section 2.2.2.2). SDF (Allen-Vanguard) is a related decontaminant with the same ingredients as CASCAD, except that a co-solvent is left out.

Chemical agents exhibit a limited solubility in water, whereas many decontaminants are highly soluble in water. Microemulsions are mixtures of water, oil, surfactants, and co-surfactants that appear as a homogeneous phase. Different water-soluble decontaminants can be dissolved into a microemulsion leading to a chemical system containing very small organic droplets dispersed into water containing the decontaminant. When a chemical agent encounters a microemulsion system, it is partially dissolved into the organic phase of the microemulsion. Once dissolved, the agent can react with the water-soluble decontaminant at the surface of the organic portion of the microemulsion [17].

BC emulsion (OWR, Elztal-Rittersbach, Germany) consists of water, xylene, NaDCC (active component) emulgator IHF, talcum and sodium chloride (or for use at low temperature calcium chloride). For training exercises a less harmful training emulsion is available. The emulsion is effective against VX, GD, HD and BWAs. The ingredients are mixed prior to use by the DEDAS system. The emulsion is in use by the Dutch Armed Forces.

The C8 emulsion (also called the German emulsion, Kärcher, Winnenden, Germany) contains $\text{Ca}(\text{OCl})_2$ as the active component. C8 is still in operation by the German Armed Forces, but is no longer produced because it is not environmental friendly.

2.2.1.3 Peroxides

Peroxides (-O-O-) are strong oxidants that offer an environmentally friendly alternative to the toxic and corroding chlorine-based decontaminants. An additional advantage is evident for the development of cold-weather solutions, since the freezing point of 50% hydrogen peroxide (H_2O_2 , H-O-O-H) is -40°C .

The oxidation of the agents HD, VX, GB and GD is shown in Figures 1 to 3 and was discussed above. Nerve agents react nearly instantaneously with the peroxy anion (OOH^-) in basic solution, to form the non-toxic alkyl methyl acids. The effectiveness increases when hydroxyl free radicals (i.e., OH^\bullet) are present. For example, non-dissociated H_2O_2 is not fully effective in detoxifying VX, as not all chemical bonds contributing to the potency of this threat agent are broken by peroxide alone.

However, hydroxyl free radicals are very effective in detoxifying VX and other chemical agents [18]. For this reason, H_2O_2 is often combined with other reagents to increase its activity and effectiveness. The oxidation of HD requires the presence of activators such as carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) or molybdate (MoO_4^{2-}). The combination of peroxide/activator oxidates HD into the non-toxic sulfoxide, and to a small extent into the toxic sulfone.

Many different formulations containing H_2O_2 have been developed and tested on BC agents. EasyDECON (also known as DF-200) is a BC decontamination technology based on H_2O_2 and surfactants that was originally developed by Sandia National Labs (Livermore, CA and Albuquerque, NM). The formula was optimized by EnviroFoam Technologies (Huntsville, AL) and is commercialized by Intelagard (Broomfield, CO) [19]. The formulation is also commercialized by Modec (Denver, CO) under the trade name Modec Decon Formula (MDF) 200 [20]. Easydecon can be dispersed as foam or in liquid form and is used by the US Armed Forces as the replacement of DS-2 (see Section 2.2.2.2). The formulations are effective against GD and VX and a number of TICs, but less effective against HD on panels. In 2003, the ground and streets of a neighborhood in Iraq that were covered with 11,000 gallons of toxic chemicals (pesticides, acids, herbicides, and organic phosphates) were successfully decontaminated by military personnel of the US Army using EasyDECON [21].

H_2O_2 is also used in the micro-emulsion Decon Green, a CB decontaminant that was patented by the Edgewood Chemical Biological Center (ECBC, Aberdeen Proving Ground, MD). The original formulation contained hydrogen carbonate as an activator. The reaction of Decon Green with HD was slow compared to the reactions with the nerve agents VX and GD [22]. The formulation was improved using the activators tetraperoxomolybdate and peroxocarbonate (catalytic, generated *in situ*) which was reported to increase HD oxidation by an order of magnitude. The improved formulation of Decon Green was also shown to be effective against *B. Anthracis* on various materials and radiological agents [23]. Decon Green is not yet commercially available.

Another peroxy compound that is commonly used, and often added as a supplemental oxidizing agent in mixtures with H_2O_2 , is peracetic acid (PAA, $\text{CH}_3\text{CO}(\text{OOH})$, or peroxyacetic acid, see Figure 5). PAA is effective against all microorganisms, including bacterial spores due to its high oxidizing potential. It can be used over a wide temperature range (0-40 °C).



Figure 5 Formation of peracetic acid and water by acetic acid and hydrogen peroxide.

PAA can be thermally stabilized by the addition of H_2O_2 , acetic acid and stabilizers to form a mixture named Wofasteril. BDS2000 is a BWA decontaminant developed by Kärcher (Winnenden, Germany) that contains Wofasteril and the buffer additive alcapur. In this solution, PAA is stabilized in a so-called solvent cage. BDS2000 can be applied as a foam for the decontamination of surfaces, or using a thermal aerosol generator (hot fogger) to clean interior spaces. BDS2000 is part of Kärcher's family of decontaminants (GDS2000 for CWA and RDS2000 for RN agents).

Oxone is a mild oxidizer that is manufactured by DuPont. The active ingredient is potassium peroxy monosulfate, KHSO_5 , which is present in a mixture with potassium sulphate salts (KHSO_4 and K_2SO_4 , in a ratio of 2:1:1) in water (see Figure 6). Oxone has been shown to effectively react with CWAs. Mechanisms for inactivation of chemical agents are less well known, but the compound is effective against both classes of agents. Lawrence Livermore National Laboratories (Livermore, CA) has developed the L-Gel system (the L is for Livermore), using Oxone with fumed silica as a gelling agent [24, 25]. The gel ensures a better cling to surfaces and can be easily vacuumed up after it has dried. L-gel is effective against CWAs and *B. Anthracis* spores and was also tested in field exercises. The product is not yet commercially available.

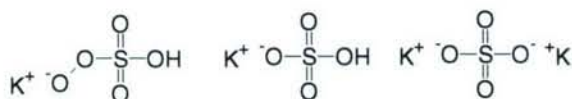


Figure 6 Oxone: a mixture of KHSO_5 (oxidiser), KHSO_4 and K_2SO_4 (in a ratio of 2:1:1).

2.2.1.4 Reactive gasses

Gaseous and vapor phase technologies have been developed for the decontamination of sensitive equipment and building interiors. The following reactive gasses will be discussed: ethylene oxide, chlorine dioxide (ClO_2), (modified) vaporized hydrogen peroxide ((m)VHP), paraformaldehyde, ozone (O_3) and methyl bromide. Most information given in this section was retrieved from [26].

The technologies are only effective against BWAs, with the exception of mVHP and aqueous ClO_2 . The degradation mechanisms are based on oxidation (e.g. ClO_2 and VHP) and alkylation (methyl bromide and formaldehyde).

The techniques require that the contaminated area is completely sealed to prevent the escape of the gas or vapor. The gas or vapor is injected into the sealed area and allowed to remain in place for the period of time required to ensure treatment. Gas and vapor

technologies are more susceptible to variations in temperature and humidity than liquid and foam technologies.

Ethylene oxide can be used for the sterilization of critical items in an off-site room, which has been done during the *B. Anthracis* letter recovery operations in the United States in 2001. Since the compound is flammable and very damaging to human health, it is not suitable for large scale use such as the fumigation of buildings.

Chlorine dioxide (ClO₂) gas reacts as an oxidizing agent and was shown to destroy BWAs. ClO₂ must be generated on site where remediation occurs using commercially available generators due to the instability of the gas. Gas replacement during remediation is required due to the instability. However, this instability has a benefit in that the gas rapidly decomposes after treatment. The gas has better penetrability than hydrogen peroxide vapor, and thus may more likely be effective on porous surfaces, although this has yet to be demonstrated. Temperature and humidity need to be controlled; effective performance may be very difficult to achieve if the relative humidity drops below 60%.

ClO₂ gas has been used in the cleanup of building interior surfaces contaminated with spores of *B. anthracis* during the remediation operations in 2001. The technology has also been shown to be capable to destroy other pathogens and viruses. The product of the concentration and contact time (Ct, ppm.hr) can be increased from 100 to 250 ppm.hr to kill the most ClO₂ resistant vegetative microorganism, *S. aureus* [27].

ClO₂ can also be used in its aqueous form. For this purpose, the compound must also be generated at the use site, typically using sodium chlorite (NaClO₂) as a reactant. No data are available for the decontamination of BWAs using aqueous ClO₂. ClO₂ is effective against HD and VX, but the technology has always been ineffective against G agents. However, Procter and Gamble (Cincinnati, OH) [28] showed that the breakdown of G agents is possible using electrochemically generated ClO₂ with nucleophilic additives.

Vaporized Hydrogen Peroxide (VHP) has been used for more than a decade to sterilize clean rooms and pharmaceutical processing equipment and, more recently, to decontaminate *B. Anthracis* contaminated buildings. The vapor is generated from a concentrated aqueous solution of hydrogen peroxide (30% H₂O₂). Typical H₂O₂ vapor concentrations (e.g., 200 ppm, or about 0.3 mg/L) might require perhaps 2 to 6 hours of contact time to destroy *B. Anthracis* spores, depending on the substrate.

STERIS Corporation (Mentor, OH) is a manufacturer of H₂O₂ vapor equipment.

The company was contracted to conduct fumigation in the remediation of two federal mail facilities following the 2001 incident. It was demonstrated to be effective against *Bacillus* spores, including the *anthracis* strain.

Modified VHP (mVHP) was developed by STERIS and the US Army ECBC (Aberdeen Proving Ground, MD). mVHP makes use of low levels of ammonia which renders the technology reactive towards CWAs (HD, GD and VX) and BWA surrogates.

Test results showed that a 24 h 250 ppm mVHP treatment decontaminated CWAs whereas a 5 h treatment was required for BWA decontamination. The technology can be used for aircraft interior decontamination and in a SED unit and is continuously being improved [29].

Paraformaldehyde is a polymerized form of formaldehyde, (CH₂O)_n. It is a stable white crystalline powder. Upon heating, it generates formaldehyde gas, which has antimicrobial properties. The technology is mature and commercially available. Paraformaldehyde is used for routine decontamination of labs and biosafety hoods in clinical and research laboratories for a broad spectrum of biological agents, including *B. anthracis* spores. Paraformaldehyde is heated to generate formaldehyde gas for use as a sterilizing agent.

This gas has been used by the U.S. military for the successful remediation of numerous laboratories and buildings. It has been used by the U.S. Army Medical Research Institute of Infectious Diseases to decontaminate buildings, and was used for treating a mail processing machine in the Department of Justice mail room following the 2001 *B. anthracis* mail attacks. Formaldehyde is an animal carcinogen and probable human carcinogen, and it is genotoxic in a number of assays.

Ozone (O₃) is a reactive form of oxygen that is a strong oxidant with documented ability to kill spores, bacteria and viruses. Ozone generation systems are commercially available. However, ozone has not been used for remediation of buildings.

The technology is promising and could be considered for further evaluation in the future.

Methyl bromide is approved for use as a pesticide under controlled conditions.

However, it is forbidden to be used on a large scale since it is an ozone-depleting compound and has potential severe human health effects. Its most common use is to kill termites in buildings, and in soil treatment for agricultural pest control. It is used as an innovative for the BWA decontamination of building interiors. Recent demonstrations show its potential for killing *Bacillus* spores [30].

2.2.2 Nucleophilic substitution

2.2.2.1 Reaction mechanism

The reaction schemes of nucleophilic substitution (hydrolysis) of HD, VX, GB and GD are shown in Figures 7 to 9. In the reaction with HD, hydroxide ions replace the chlorine atoms producing hydrochloric acid and the relatively non-toxic hydrolysis products thiodiglycol (TDG) and TGD sulfoxide (see Figure 7A). Strong bases such as DS-2 (see Section 2.2.2.2) lead to the formation of thioalkenes (see Figure 7B). In the reaction with GB and GD (Figure 9), the hydroxide bond disrupts and breaks the P-F bond and forms a P-O bond. The hydroxide ion is not as effective for VX as it is for G-agents. In VX, the critical bond is the P-S bond. While the hydroxide ion will break the P-S bond, there is a competing reaction that replaces the ethoxy group with a hydroxyl group, forming desethyl-VX, also known as EA 2192 (Figure 8). This compound is comparable to VX in its toxicity. Depending on the conditions, up to 14% of EA 2192 will be produced. In addition, the solubility of VX in a basic solution is low, which will affect the reaction rate at low (room) temperature.

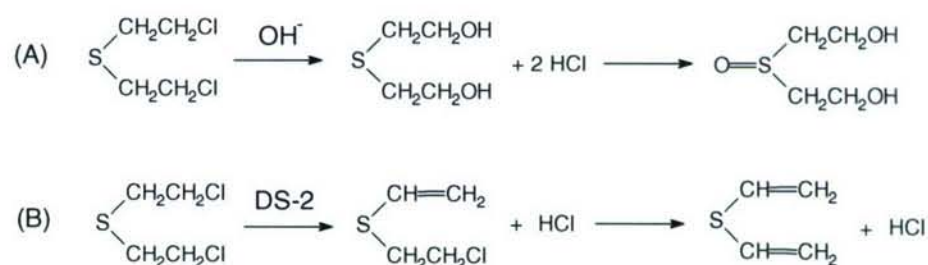


Figure 7 Hydrolysis of HD: A) by a hydroxide anion into thiodiglycol (TDG) and TGD sulfoxide and B) by DS-2 into thioalkenes.

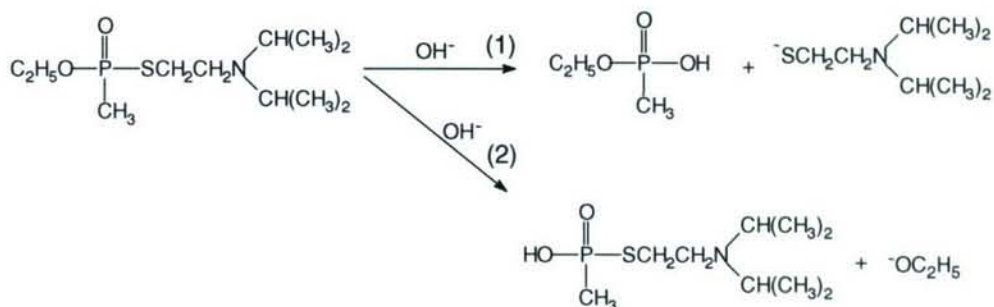


Figure 8 Alkaline hydrolysis of VX (pH 13) into (1) ethyl methyl phosphonic acid (EMPA) and 2-(diisopropylamino) ethanethiol (DIASH) or (2) EA2192 and ethanol.



Sarin (GB): R = (CH₃)₂CH

Soman (GD): R = (CH₃)₃CCH(CH₃)

Figure 9 Hydrolysis of sarin and soman into isopropyl methylphosphonic acid (IMPA) and pinacolyl methylphosphonic acid (PMPA), respectively.

2.2.2.2 Alkaline hydrolysis

Strong bases, such as calcium hydroxide CaO, Ca(OH)₂, sodium hydroxide (NaOH), and potassium hydroxide (KOH), produce a high concentration of hydroxide ions upon mixing with water. These compounds, when in solution, are effective in hydrolyzing chemical agents. NaOH is the most widely used base in a solution since it has the highest solubility of these compounds.

Strong bases such as NaOH can also dissolve into an organic solvent forming a very strong basic solution. Upon mixing of a strong base with an alcohol, the conjugate base of the alcohol or alkoxide (R-O⁻) is formed.

The most well known member of this technology is Decontaminating Solution Number 2 or DS-2. DS-2 is recognized as the military bench mark for effective BC decontamination. It reacts instantly with the G agents, VX, and HD at ambient temperatures. The solution is made up of 70% diethylenetriamine (DETA), 28% 2-methoxyethanol (also known as ethylene glycol monomethylether, EGME), and 2% NaOH [14, 17, 26]. In this solution, NaOH reacts with EGME to form ethoxide. As DETA is added, free sodium ions are rapidly bound in the mixture. This causes the hydroxide ions to be highly reactive, effectively increasing the strength of the basic solution.

DS-2 was formulated to be a general purpose reactive decontaminant that would be ready to use over a large temperature range, and have long-term storage stability. DS-2 is noncorrosive to most metals, but it can damage paints, plastics, rubbers, and leather materials. DS-2 is flammable and cannot be used in conjunction with strong oxidizing agents such as bleach, which cause it to spontaneously combust. DS-2 is no longer manufactured and is not used at chemical agent destruction facilities because of its corrosive nature to rubber, paint and plastics and its environmental effects. Most nations, including The Netherlands, have recently replaced DS-2 or are in the process of replacing the decontaminant.

Another non-aqueous decontaminant based on alkoxides is GDS2000 (Kärcher, Winnenden, Germany). Its components are diethylenetriamine, aminobutanol and NaOH. It is a ready-to use decontaminant that is very reactive towards all known CWAs (including thickened agents) within the temperature range of $-30\text{ }^{\circ}\text{C}$ to $+49\text{ }^{\circ}\text{C}$. GDS2000 has been chosen as the replacement of DS-2 in The Netherlands and several other countries such as Belgium. The decontaminant is not effective against BWAs. Kärcher has developed other decontaminants against BW agents (BDS2000) and radiological contaminants (RDS2000).

GD-5 (OWR, Elztal-Rittersbach, Germany) was developed for BC decontamination of sensitive equipment, vehicles, airplanes and their interior and exterior. The decontaminant contains potassium hydroxide (KOH) in combination with organic solvents (aminoethanol, benzylalcohol and propanol). GD-5 is a fogging agent that is premixed and ready to use. The Dutch Armed Forces uses GD-5 in combination with the Decofogger. In a study towards the decontamination of aircraft interiors, it was shown that GD-5, nebulised by the Turbofogger, is a better nerve than blister agent decontaminant [31]. OWR's R&D program has developed a new decontamination solution, GD-6, which has a similar composition to GD-5 but is more effective in decontaminating HD.

2.2.2.3 Oximes

Oximes are known for their therapeutic use of nerve agent poisoning, acting as reactivators of inhibited acetylcholinesterase [32]. These oximes comprise of one or two quarternary amines and one or two oxime moieties ($-\text{C}=\text{N}-\text{OH}$), such as obidoxim, HI-6, and pralidoxime (2-PAM). Oximes are also used for (skin) decontamination. Figure 10 shows the degradation of GB by 2,3-butanedion-monooxime.

Oximes are used as the active ingredient in the Canadian skin decontaminant RSDL (reactive skin decontamination lotion). RSDL was purchased by the Dutch Armed Forces as a fielded skin decontaminant after extensive studies performed at TNO in the mid-nineties of the previous century to investigate whether a suitable commercially available alternative to Dutch Powder existed [33-34]. RSDL appeared to be the best overall performing skin decontaminant. It was by far the most effective decontaminant for VX. RSDL also performed very well against lewisite, but its efficacy against unthickened sulphur mustard in the *in vivo* experiments was not impressive. Recently, a modified version of RSDL from E-Z-EM, Inc. (Lake Success, NY) exhibited improved efficacy for HD and good efficacy for acid TICs [35]. RSDL is also being investigated by Batelle (Aberdeen, MD) for the decontamination of individual equipment and weapons [36].

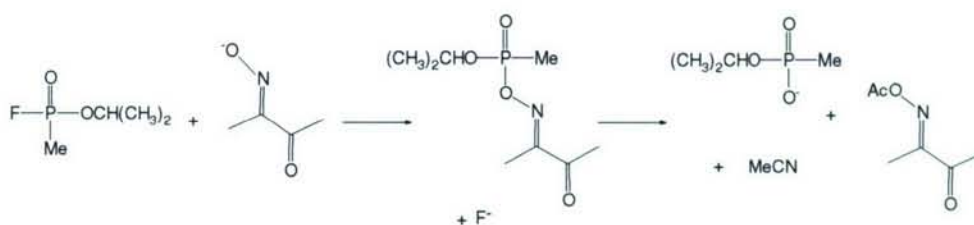


Figure 10 Degradation of sarin by 2,3-butanedion-monooxime.

2.2.3 *Alternative chemical approaches*

2.2.3.1 *Metal ion catalyzed hydrolysis*

Several metal ions and their complexes (such as Cu^{2+} , UO_2^{2+} , ZrO^{2+} , MoO_2^{2+} , Th^{4+} , Mn^{4+}) have the ability to catalyze the hydrolysis of G agents (GB and GD) [14].

Two mechanisms for the activation step are possible. The catalytic species could be the hydroxometal complex (eg CuOH^+), or the metal ion could act as a Lewis acid by complexing with the substrate at the phosphoryl oxygen followed by attack of the hydroxide ion on the GB-Cu complex. As in the case of GB, the rate of GD hydrolysis is accelerated by 1 order of magnitude in the presence of 0.001 M CuSO_4 at 25 °C. When CuSO_4 is increased to 0.01 M, the reaction becomes too fast to be followed under the same conditions [14]. Metal ions do not accelerate the hydrolysis of VX and HD due to the formation of unfavourable complexes. For this reason, the applicability of metal ion decontamination for an operational setting will be limited.

2.2.3.2 *Reactive sorbents*

A reactive sorbent first adsorbs the BC contaminant and then chemically detoxifies it. Reactive sorbents have been prepared by soaking simple sorbents in alkaline solutions, effectively 'loading' the matrix with caustic material. Once sorbed into the sorbent matrix, the agent encounters the alkaline medium, reacts with it, and is destroyed. A second approach for reactive sorbents is to prepare a polymeric material with reactive groups attached to the polymeric backbone. In this case, the agent is sorbed by the polymeric matrix, encounters the reactive group, and is neutralized by it. A third approach is to use microcrystalline metal oxides such as aluminum oxide or magnesium oxide. An example of decontamination equipment utilizing reactive sorbents is the Decontamination Kit, Individual Equipment: M295, manufactured by Trueteck (Riverhead, NY).

Catalytic sorbents are similar to reactive sorbents in that both contain reactive sites that react with and detoxify the BC contaminants. In the case of catalytic sorbents, the reactive site is regenerated during detoxification of the agent while, in the case of reactant sorbents, the reactive group is rendered inert after reacting with the agent. Examples of catalytic sorbents are polyoxometalates sorbed into a sorbent polymeric matrix and polymeric materials containing reactive sites that are covalently bound to the polymer chain.

2.2.3.3 *Nanoactive particles*

FAST-ACT (NanoScale Materials, Inc., Manhattan, KS) is a formulation based on nanoparticles containing 'nanoactive' titanium dioxide and magnesium oxide [37]. Nanoactive materials are novel forms of metal oxides that possess extremely high surface areas. The dry powder is claimed to be effective for neutralizing a wide range of TICsF in either liquid or vapor form, with the added capability to destroy chemical warfare agents. Reactive nanoparticles adsorb toxic compounds, but also chemically dismantle them. The formulation is safe, non-toxic, non-flammable, and non-corrosive. FAST-ACT's effectiveness has been verified against GD, VX and HD by two independent laboratories as shown on the companies website [37]. FAST-ACT destroys CWAs through hydrolysis and dehydrohalogenation. Nerve agents (VX and GD) are hydrolyzed with the formation of surface bound metal phosphonates. It should be noted that during this reaction the toxic EA-2192 does not form, in contrast to basic VX hydrolysis in solution. HD undergoes hydrolysis to form surface bound metal alkoxides. The dehydrohalogenation products, vinyl and divinyl HD are not bound to the surface and thus remain volatile.

2.3 Enzymatic decontamination

An environmental friendly alternative of aggressive chemical decontaminants was found in enzymes. Most research has been performed towards G-type nerve agent destructing enzymes, however, some enzymatic approaches towards destruction of VX, HD and BWAs have been reported.

The enzymatic decontamination of organophosphate (OP) nerve agents can be accomplished by two enzyme categories: scavengers and OP hydrolyzing enzymes [38]. Scavengers are proteins that covalently bind OPs. Naturally occurring human proteins that function as scavengers are acetylcholinesterase, butyrylcholinesterase and carboxylesterase. A disadvantage of scavengers is that one molecule of protein has the capacity to bind and thereby eliminate only one OP molecule. The enzyme becomes inactive after detoxifying the nerve agent and is thus consumed. Like scavengers, OP hydrolyzing enzymes (also known as phosphotriesterases) bind with OPs, but this is followed by spontaneous reactivation of the enzyme-OP complex. As a result, a non-toxic hydrolysis product (alkyl methyl phosphonic acid) is released and the enzyme activity is restored. OP hydrolases have been identified with catalytic activity towards various OPs that contain P-O, P-F, or P-CN bonds. However, it was observed that OPs containing a P-S bond, such as VX, are more resistant to enzymatic hydrolysis.

Enzymatic decontamination systems have been developed and tested successfully against chemical agents by researchers at ECBC (Aberdeen, MD). OP hydrolyzing enzymes were reported to be incorporated into sponges for skin decontamination [39] and into fire fighting foams [40]. In 2004, a collaboration between ECBC and Genencor International (Palo Alto, CA) resulted in the commercialization of a line of decontaminants under the trade name DEFENZ™ [41]. DEFENZ is an environmentally friendly decontaminant that is capable of breaking down specific OP (G-type) agents. It is available in a powder form that requires the addition of water for decontamination. On-going research is focused on the development of enzymes for the (improved) enzymatic degradation of VX, HD and BW agents. Attempts are being made to modify the cloned gene of enzymes, to change the catalytic specificity and to increase the ability to degrade OPs. In the search for a HD degrading enzyme at ECBC, an enzyme was derived from a *Rhodococcus* bacterium with catalytic activity with HD as the substrate. The enzyme has previously been characterized as a hydrolytic dehalogenase and apparently catalyzes the hydrolysis of HD, because chloride is released stoichiometrically. Another approach is the use of chloroperoxidase, an enzyme that produces H₂O₂ and chlorine in the presence of urea H₂O₂ and sodium chloride (enzymatic haloperoxidation). This enzyme was shown to degrade VX and HD [42].

Enzymatic destruction of BWAs can be accomplished by two other classes of enzymes. The enzymes alcohol oxidase and chitinase have been shown to possess sporicidal and bactericidal activity. Alcohol oxidase oxidizes primary alcohols creating the aldehyde of the alcohol and H₂O₂. Enzymatically-generated H₂O₂ also offers potential for CWA decontamination. Chitinase has degradative activity on β -1-4-petidoglycan linkages. The enzymes are being investigated at the US Army RDECOM (Aberdeen Proving Ground, MD) and Geo-Centers, Inc (Newton, MA).

Genencor International reported a study towards perhydrolase, an enzyme which produces peracetic acid from H₂O₂ and acetic acid esters [43]. Perhydrolase is the product of extensive protein engineering and is a stable enzyme with a broad pH range. All-Clear (US Global Nanospace, Inc. (Mansfield, TX), supplied by Kidde Firefighting (Angier, NC)) is the only decontaminant formulation that utilizes an enzyme and biocide foam mixture, making it effective against nerve agents and BWAs (spore and

non-spore, including *Bacillus anthracis*), viral agents (e.g. Avian Flu) and toxins [44] within one hour of application. For inactivation of nerve agents, All-Clear utilizes the OP hydrolyzing enzymes as developed by ECBC. All-Clear contains organic solvents within its formulation which are considered key to the inactivation of HD. Degradation of HD is being further investigated.

2.4 Directed energy decontamination

Directed energy methods for decontamination, such as photochemical, ultra violet radiation, plasma, and microwave radiation have all been demonstrated to disinfect surfaces. As energy transfer methods, all of these systems can kill bacteria, bacterial spores, and viruses, given sufficient time and power.

Clean Earth Technologies (St. Louis, MO) uses a photochemical process and developed the Electrostatic Decontamination System (EDS) [26]. Their two step process is claimed to work on BC agents including TICs. The EDS is configured with a photosensitizer sprayer unit, a photosensitizer storage unit, and a light source unit (210 – 310 nm UV light source) for activation. The photosensitizer is sprayed onto the surface from a distance of 24 inches, and the UV light can reportedly then decontaminate approximately 1,000 square feet of surface area in 15 minutes. The system has been tested on vertical, horizontal, porous, and non-porous surfaces. The photosensitizer solution is claimed have a shelf life of 10 years and is non-corrosive. This technology is still subject to research and is not commercially available.

Plasma is defined as a energetic collection of ionized particles (electrons, ions, and radicals) that exhibit a collective behavior due to electromagnetic forces.

Atmospheric plasma decontamination (APD) can be applied for the destruction of biological organisms. By passing energy through air, the molecules are ionized generating both positively and negatively charged reactive species. The interaction of these ions, along with the associated ultraviolet light, kills the microorganisms. APD is applicable to the cleaning, and perhaps disinfection, of small areas and electronic equipment. The technique is being investigated by AGT (Knoxville, TN) as a means to neutralize BW agent contaminated aircraft cargo and interiors [45].

A high-powered plasma arc lamp fitted with a large area reflector was developed at Oak Ridge National Laboratory (Oak Ridge, TN) and shown to kill *B. Globigii* spores in less than 7 seconds [46]. The utility of this method is further realized in its ability to be mounted on a remotely operated robotic platform.

A microwave reactor was developed by CHA Corporation (Laramie, WY) [47-49] for the destruction of CWAs in rinsing water of military vehicles. In addition, it is mentioned that the microwave process combined with granular activated carbon has a strong potential to destroy BWAs in water. The decontamination potential of the microwave technology for BC agents will be studied at TNO Defense Safety and Security in the near future.

3 Concluding remarks

This report outlines the current state of the art of CBRN decontamination technologies up to January 2007. It was shown that many different approaches have been developed for the removal and destruction of CBRN agents. It is clear that there is no single, ideal decontaminant suitable for clean-up of every agent in every operational situation. The choice of a decontamination method depends on various factors, mainly being the type of agent, the contaminated object (e.g. a military vehicle, sensitive equipment or building interior), and the operational situation and location (e.g. remote area or homeland city).

Basically, decontamination technologies can be divided into four basic processes: physical, chemical, enzymatic and energetic. Physical removal or encapsulating of agents can be an easy, quick, yet inadequate solution after a CBRN incident. Besides weathering (natural evaporation), the contaminant can be rinsed off with water or cleaned-up by adsorbents. A more advanced technology is the use of strippable coatings for either the containment or removal of agents. Decontamination of RN agents is in principle achieved by physical removal using decontaminants that contain surfactants and complexants. The most common and effective technology is the use of chemical decontaminants that actually destruct BC agents. Formulations consist of aqueous or organic solutions, micro-emulsions, foam or powder. Many formulations with different chemicals have been developed, but no single decontaminant is able to effectively destruct every BC agent. Well known are the oxidative decontaminants based on chlorine. An example is the BC emulsion that contains NaDCC as the active component. Chlorine based decontaminants are effective but also corrosive. Peroxide containing decontaminants are an environmentally friendly alternative. Hydrogen peroxide (H_2O_2) is effective against nerve agents, but requires additives to catalyze the destruction of HD. Peracetic acid (PAA) is a peroxy compound that is effective against BWAs.

Reactive gasses are commonly used for the decontamination of (building) interiors, but some are very toxic. The most potential reactive gas seems to be modified Vaporized Hydrogen Peroxide (mVHP), which is effective against CWAs (HD, GD and VX) and BWA surrogates.

As an alternative to oxidation, hydrolysis of CWAs can be achieved by strong bases in water or organic solvents. Examples are DS-2, GD-5 and GDS2000. DS-2 is highly effective but is currently being replaced by most nations due to its high toxicity. GDS2000 is the decontaminant that has been chosen as the replacement of DS-2 in The Netherlands. It is effective against CWAs but was not developed for the destruction of BWAs. Therefore, in addition to GDS2000, decontaminants against BWAs (e.g. BDS2000) and RN agents (e.g. RDS2000) need to be available.

More environmentally friendly, but less far in development are enzymatic decontaminants. Most research has been performed towards G-type nerve agent destructing enzymes, however, some enzymatic approaches towards destruction of VX, HD and BWAs have been reported. The problem remains that there is no single enzyme suitable for destruction of all BC agents, so that enzymes need to be mixed to be effective against more types of agent. Since several years, two commercial decontaminants based on enzymes are commercially available.

Finally, directed energy methods for decontamination include photochemical, ultra violet radiation, plasma and microwave radiation. These methods have been demonstrated to disinfect surfaces, but are not generally applicable.

In conclusion, CBRN decontamination is a broad and interesting research area, which holds sufficient challenges to inspire researchers for new developments in the future.

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5 Signature

Rijswijk, March 2007

TNO Defence, Security and Safety

A handwritten signature in blue ink, appearing to read 'S. van der Gijp'.A handwritten signature in blue ink, appearing to read 'C.M. Boone'.

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